

1

2,990,245

METATHESIS OF BISMUTH PHOSPHATE PLUTONIUM CARRIER PRECIPITATE WITH AN ALKALI

Isadore Perlman, Berkeley, Stanley G. Thompson, Richmond, and Burris B. Cunningham, Berkeley, Calif., assignors to the United States of America as represented by the United States Atomic Energy Commission

No Drawing. Filed Apr. 30, 1947, Ser. No. 745,108
11 Claims. (Cl. 23—14.5)

This invention relates to a method of separating plutonium from contaminating elements and more specifically is concerned with a process for concentrating plutonium during separation from contaminating elements.

The word "plutonium" as used in this specification and claims refers to the element with atomic number of 94 and to compositions containing this element unless the context indicates the elemental or metallic form.

Plutonium is usually produced by the reaction of neutrons with uranium, a reaction ordinarily carried out in a pile. The uranium mass as removed from the pile is comprised principally of unreacted uranium, but there are very small amounts of neptunium, plutonium and radioactive fission products present. Neptunium is radioactive and has a half-life of only 2.3 days decaying to plutonium by beta ray emission. Substantially all of the neptunium in the uranium mass, therefore, may be converted to plutonium by suitable aging of the mass for a few weeks.

A common method of separating plutonium from the uranium and other contaminants contained in the uranium mass following aging, is the bismuth phosphate-lanthanum fluoride precipitation process. This process may be arbitrarily divided into four steps: (1) Extraction, in which plutonium and some fission products are separated from uranium and the bulk of the fission products; (2) Decontamination, in which plutonium is separated from the remaining fission products; (3) Concentration, in which the ratio of plutonium-to-carrier is increased sufficiently that the plutonium may be precipitated directly from solution; (4) Isolation, in which the plutonium solution is further concentrated.

In order to carry out the extraction step, the uranium mass after suitable aging is usually dissolved in a concentrated aqueous nitric acid solution, to produce a uranyl nitrate hexahydrate solution. This solution is then diluted with water to give a uranyl nitrate hexahydrate solution of about 20% concentration. This dilute solution is contacted with a suitable reducing agent to insure that all of the plutonium ions are in the quadrivalent state. Sulfuric acid or a soluble sulfate is also added to the solution to complex the uranyl ions and prevent their precipitation in the subsequent steps. A precipitate of bismuth phosphate is then formed in the solution and separated therefrom. This bismuth phosphate precipitate carries with it the plutonium and certain of the fission products, which form insoluble phosphates, particularly zirconium and niobium. In the decontamination step this bismuth phosphate carrier precipitate containing plutonium and phosphate insoluble fission products is dissolved in a concentrated inorganic acid, usually a 60% nitric acid, and the acid solution then diluted with water to about a 5 N acid solution. The plutonium ions are then oxidized to the hexavalent state in which state plutonium is soluble as the phosphate. A bismuth phosphate precipitate is formed in the oxidized solution and separated therefrom carrying with it the phosphate insoluble fission products. The hexavalent plutonium ions are then reduced to the quadrivalent state and the solution is diluted so that the acidity is approximately 1 N. A bismuth phosphate carrier precipitate is then formed in the solution and separated therefrom carrying with it the plutonium. This de-

2

contamination cycle may be repeated as often as necessary to insure complete separation of the plutonium and the fission products. Following the decontamination step, the concentration and isolation steps are carried out.

One of the disadvantages of the present method of separation is the large, dilute acid-to-plutonium ratio at which the plutonium precipitations in the decontamination step are carried out. The bismuth phosphate precipitate is difficultly soluble in nitric acid and it requires a large amount of concentrated nitric acid to dissolve the bismuth phosphate carrier cake. This volume of solution is then greatly increased by the necessity of carrying out the plutonium precipitation step from the solution at not appreciably greater than 1 N acid concentration. If the acid concentration is increased much above 1 N, there is a strong tendency for the acid to oxidize the plutonium to the +6 valence state in which state plutonium is soluble in the phosphate solution. Because of the difficulty of dissolving the bismuth phosphate and the necessity of diluting the acid solution to approximately 1 N, it is impossible to concentrate the plutonium in the decontamination step as it is presently carried out, since the amount of acid solution from which a plutonium precipitation step is carried out is approximately the same as the amount of acid solution in the preceding step.

A procedure whereby the bismuth phosphate cake would be dissolved to furnish a 1 N acid solution containing plutonium and the volume of the solution is smaller than the volume of the preceding 1 N acid solution from which the bismuth phosphate carrier cake was precipitated, would greatly increase the efficiency of the present bismuth phosphate separation process in many ways. For example, a much larger uranyl nitrate hexahydrate batch could be processed at one time. The amount of storage space required for the highly radioactive waste could be greatly reduced. The amount of separation process reagents used in steps subsequent to the decontamination cycle would be greatly decreased, and the waste losses of plutonium in the subsequent steps could be kept at a minimum by operating at the minimum practical volume. It can be readily seen that there are numerous other advantages.

One object of this invention is to effect a concentration of plutonium as a salt in an aqueous solution.

An additional object of this invention is to effect an improvement in the bismuth phosphate-lanthanum fluoride-plutonium separation process whereby the ratio of plutonium to plutonium carrier may be greatly increased in the extraction and decontamination steps of that process.

Still other objects of this invention will be apparent from the description and claims which follow.

We have discovered that a bismuth phosphate carrier precipitate containing plutonium may be converted into a bismuth hydroxide carrier precipitate containing plutonium, and that the hydroxide may be dissolved in a much smaller quantity of an inorganic acid than the bismuth phosphate carrier could be, and then diluted to furnish a dilute acid solution containing plutonium. Broadly, the process of our invention comprises the treatment in an aqueous medium of a bismuth phosphate carrier precipitate containing plutonium with a material of the group consisting of water-soluble, carbonates, bicarbonates, and hydroxides, and mixtures thereof, for the purpose of converting said bismuth phosphate carrier precipitate to the hydroxide, separating this hydroxide-plutonium carrier from the aqueous medium and dissolving said hydroxide carrier in a suitable acid, such as nitric acid.

Suitable reagents for the conversion of the bismuth phosphate to the hydroxide include the carbonates, bicarbonates, and hydroxides of the alkali metals. The hydroxides of these metals are preferable to the carbon-